

PATENT SPECIFICATION

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(54) A PROCESS FOR INCREASING THE HYDROPHILIC
CHARACTER OF FIBROUS MATERIALS OR PRODUCTS
PREPARED THEREFROM

(71) We, TEXTILIPARI KUTATO
INTEZET, a Hungarian Body Corporate, of
Gyomroi u. 86, Budapest X, Hungary, do
hereby declare the invention, for which we
pray that a patent may be granted to us, and
the method by which it is to be performed,
to be particularly described in and by the
following statement:—

This invention relates to a process for im-
10 proving the properties of fibrous materials,
including products prepared therefrom, by
forming active centres on the material or
product to be treated, grafting in an aqueous
15 solution of a monomer containing an acryl
group at a temperature below 100°C and
washing the product obtained.

It is known that the properties of macro-
molecular substances of natural, regenerated
20 or synthetic origin may be altered by graft-
ing. This procedure is generally carried out
by linking one or more monomers or sometimes
also oligomers or polymers of suitable
25 characteristics to the macromolecule to be
grafted. Grafting is principally initiated with
chemical agents or by irradiation methods.

It is also well known that initiation may
be carried out simultaneously with or prior
30 to grafting. If initiation precedes grafting,
usually only one of the components to be
grafted is subjected to the initiation effect.

Grafting may be carried out both in homo-
geneous and in heterogeneous systems. In the
35 case of a homogeneous system, e.g. when both
the component to be grafted and the com-
ponent to be applied are in the liquid phase,
a grafted product of uniform quality can be
obtained. If grafting is carried out in a
40 heterogeneous system—e.g. when the sub-
stance to be grafted is in the solid phase,
while the component to be applied is in the
liquid or gaseous phase—grafted copolymer
is generally formed only on the surface of the
45 component to be grafted. If cross-grafting is
to be carried out, the solid component is
generally used in swollen state.

The grafting process may be regarded as

a special case of copolymerization, wherein a
copolymer is formed that contains the grafted
component or components not in the chain
but in the form of branches or terminal
moieties. As an undesired by-product, a cer-
tain amount of homopolymer is also formed
in the grafting process.

It is known that, in order to make graft-
ing realizable on an industrial scale, efforts
should be made to avoid the formation of
homopolymers (Melliand Textilberichte, 49,
99/1968/).

As has been mentioned, above, the aim of
grafting is to provide the substances with
new and favourable properties, or to avoid or
reduce their existing disadvantageous char-
acteristics, respectively. Several processes
have been developed for changing or improv-
ing e.g. the adhesive properties, weather-
resistance, resistance to microorganisms, dye-
ability, hydrophilic, hydrophobic, oleophilic
or oleophobic character respectively of the
substance to be grafted. According to a known
process for improving the hydrophilic pro-
perties of substances, monomers of hydro-
philic character are linked by grafting to the
substance or component to be grafted. A dis-
advantage of this known process is the occur-
rence of the so-called gel-effect. This effect,
as it is described on page 19 and subsequent
pages of the monograph "Fibres from Syn-
thetics Polymers" by R. Hill (Elsevier Pub-
lishing Co., Amsterdam—Houston—New
York—London, 1953), consists mainly in that
the viscosity of the solution increases sim-
ultaneously with the progress of the polymeriza-
tion, and at the end the solution even solidi-
fies; the rapid increase of the viscosity, in
turn, increases the polymerization rate, since
the chain-termination process is repressed.
According to Hill the gel-effect also increases
the reaction rate in the case of heterogeneous
polymerization. The increase of viscosity re-
tards the reaction between the large molecules
by blocking molecular motion; it does not,
however, influence the reactivity of mono-

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mers of lower molecular weight, since the diffusion of the latter is not hindered.

British Patent Specification No. 809,838 relates to grafting initiated by preliminary irradiation. In Example 5 of the above patent specification it is mentioned that, when acrylamide is used as the grafting monomer, the solution becomes highly viscous due to the formation of polyacrylamide homopolymer.

- 10 This has a detrimental effect on the grafting of acrylamide on polyethylene. Example 8 relates to the grafting onto cellulose acetate of acrylamide; according to this process the polyacrylamide by-product is separated from the grafted product by swelling. Example 9 of the above patent specification discloses the grafting of acrylamide onto polymethylmethacrylate films. The formation of large quantities of polyacrylamide was observed also in this process. The homopolymerization of the monomer used for grafting renders the process very disadvantageous from the economic point of view.

S. Okamura et al ("Large Radiation Sources in Industry Proceedings on the Conference held in Warsaw", 1959, Vol. 1, pp. 459 to 470) reported that, if the system is irradiated prior to grafting and a subsequent irradiation is also carried out, acrylamide can be grafted onto nylon in methanol only with a total yield of 8.6%. In this case also, the poor yield was due to the formation of substantial amounts of acrylamide homopolymer.

In the processes mentioned above, the length of the grafting period ranged between 20 and 72 hours and the dosage of the preliminary irradiation ranged between 2.3 to 16.2 Mrad. In some instances shorter grafting periods were applied; in these cases, however, the dosage required for initiation substantially damaged the polymer to be grafted. Grafting was carried out in several cases at temperatures exceeding 130°C and, accordingly, the process was to be carried out in pressure-tight equipment. In the course of grafting the substance sinters considerably. In several cases, at the end of the process, the surface of the substance was reduced to 20% of the original value.

50 The common drawbacks of the known processes are the following: the processes are generally complicated, the treatment is time-consuming or the processes are uneconomical due to the formation of homopolymers, or 55 they are not suitable for industrial purposes at all, because of the rigidity, sintering or deformation of the products. It is just for these reasons that neither literary references nor patent specifications relating to grafting 60 describe in detail the properties of the products obtained. So, for example, even if it is said that on grafting the dyeability of the product is improved, no mention is made of the tensile strength, dimension stability, elasticity, flexibility, handle, etc. of the product.

A further drawback of the known processes is that, mainly due to the increase of viscosity caused by the gel-effect, products of uniform quality cannot be obtained, since, in the system of increased viscosity, the diffusion rate of the component used for grafting to the component to be grafted is not uniform.

70 The object of the invention is to avoid the disadvantages of the known methods and to provide a process which allows the production of substances of high quality even on an industrial scale.

This invention is based on the discovery that if the fibrous materials, including products prepared therefrom, containing active centres are grafted in an aqueous solution of the hydrophilic monomer containing the components used for grafting in the form of a monomer and/or aggregates of monomer, the viscosity of which solution is at least 1.2 cP at 20°C and at a shear stress of 10 g/cm² and not more than 300 cP at 20°C temperature and at a shear stress of 50 g/cm², the properties of the fibrous materials can be permanently improved by grafting and the process can be carried out practically without any formation of homopolymer.

90 The invention is based further on the discovery that the above grafting process can be carried out in a particularly advantageous manner if the substance is moved during grafting without damaging the gel-structure formed in the solution of the monomer.

95 We have finally found that the solution of the monomer obtained after grafting can be repeatedly used for grafting without any qualitative change, only by supplying additional amounts of the applied monomer, the evaporated water and the other additives optionally present. This fact is very surprising, since up to now it has been believed that 100 the increase of the viscosity of the monomer solution during grafting, i.e. the gel-effect, is due to the formation of homopolymer, and for this reason the solution cannot be repeatedly used (see e.g. the Examples of British Patent Specification No. 809,838).

105 Thus, the present invention consists in a process for treating a fibrous material by forming active centres on said material and grafting onto said material a monomer containing an acryl group by moving said material through an aqueous solution of said monomer at a temperature below 100°C without damaging the gel structure formed in the solution and while applying a shear stress not greater than 300 g/cm², the solution having a viscosity of at least 1.2 cP at 20°C and at a shear stress of 10 g/cm² and not more than 300 cP at 20°C and at a shear stress 110 of 50 g/cm².

115 After grafting, the monomer, water, and optional additives, if any, may be replenished and the solution reused for a subsequent grafting process or processes.

5 A certain amount of gelling necessarily takes place, even in the process of the invention; this is not, however, due to the formation of homopolymer, but is due to structural gel formation, which can be eliminated at any time by simple physical means, e.g. by shaking, vibration or stirring.

10 This reversible gel formation is influenced by several parameters, such as the concentration of the solution, the weight ratio of fibrous material to monomer solution, the activation dosage, the temperature prevailing in the course of the grafting reaction, the duration of the process, and the speed of moving. The concentration and the weight ratio of fibrous material to monomer solution preferably vary within a certain range.

15 As has been mentioned above, the speed of moving and the corresponding shear stress may not exceed a certain upper limit.

20 The concentration and the weight ratio of fibrous material to monomer solution are correlated. For example, if the concentration of the solution is 50 g/l., the weight ratio of the fibrous material to be grafted to the monomer solution is preferably at least 1:40 and, for best results, may not exceed the value of 1:100. If a lower ratio (e.g. 1:20) is used, the solution thickens during grafting to such an extent that homopolymer is also formed and the yield of grafting decreases. On the other hand, if a higher (e.g. 1:150) ratio is used, gelling takes place to a very small extent, if at all, and the material is not grafted to the extent required in practice.

25 The main advantages of the process according to the invention are the following:

30 a) As homopolymer-formation is avoided, the yield of the process is very advantageous.

35 b) By enrichment of the bath after grafting, it can be repeatedly used.

40 c) The invention makes it possible to improve the equilibrium sorption of atmospheric humidity and the water-retaining capacity of fabrics made of hydrophobic or substantially hydrophobic fibrous materials, e.g. of polyamide fibres; accordingly the clothing-physiological properties of the fabrics can be modified as desired.

45 d) The dimensional stability of the grafted products is improved in all cases.

50 e) The crease-recovery properties of the fibrous materials may also be improved by grafting with a suitable acryl derivative.

55 f) The dyeability of the grafted products improves and, accordingly, they may be dyed with less expensive dyestuffs.

60 g) When polyamide is grafted, the melting-point of the product increases and the product becomes more acid-proof.

The invention is further illustrated with reference to the following Examples.

Example 1

10 g. of polyamide 6 (Danamid) multifilament fibrous material were irradiated with a 1.5 Mrad dosage of γ -radiation from a Co⁶⁰ source. The irradiated material was put into an aqueous acrylamide solution, and the air was expelled from the system by filling up with liquid. The concentration of the acrylamide solution was 50 g/l., the weight ratio (fibrous material:solution) was 1:60, and the initial viscosity of the solution was 1.2 cP (at 20°C at a shear stress of 10 g/cm²). The bath was heated to 94±3°C, and the fibrous material was moved in circles for 3 hours at a speed of about 5 m/min. (shear stress: 105 g/cm²). Thereafter the material was removed from the bath, washed and dried.

15 The weight of the product obtained had increased by 55 to 60%, this weight increase corresponding to the extent of grafting. Its equilibrium sorption of atmospheric humidity was 9% (at 20°C and at 65% relative humidity). The water-retaining capacity of the product was similar to that of cotton, and the product was easily dyeable with dyestuffs ordinarily used in the industry. These properties of the product remained unchanged even after 60 washings. Compared to the starting material, the tensile strength of the product remained practically unchanged.

20 Since in the course of grafting a part of acrylamide present in the bath was removed by the product, the acrylamide content of the bath decreased. The viscosity of the spent bath was 56 cP (at 20°C and at a shear stress of 20 g/cm²). The structural viscosity of the bath was eliminated by vigorous stirring, and thereafter the amount of acrylamide corresponding to the loss was dissolved in the bath. When the grafting process was repeated using a bath prepared as described above, a product of the same quality as in the first process was obtained. This procedure can be repeated practically any number of times. After the 18th repetition of the process the viscosity of the bath was 272 cP (at 20°C and at a shear stress of 50 g/cm²).

Example 2

Polyamide 6 (Grilon, Emser Werke, Switzerland—"Grilon" is a Registered Trade Mark) monofilament fibres of 0.1 mm diameter were irradiated with 0.3 to 0.5 Mrad dosages of γ -radiation from a Co⁶⁰ source. The activated fibres were placed into an aqueous acrylamide solution (concentration: 50 g/l, weight ratio fibres:solution 1:20). Thereafter the fibres were grafted and processed as described in Example 1.

25 The weight of the product obtained had increased by 45%. Its equilibrium humidity content was 9%. The product was easily dyeable according to the usual dyeing methods of the textile industry.

Example 3

Polyamide 6 (Lilion; Rhodiacet, Italy—"Lilion" is a Registered Trade Mark) multi-filament fibrous material was activated with a 5 3.5 Mrad dosage of β -radiation arising from an electron accelerator of 1.5 MeV energy. The fibres were grafted and processed as described in Example 1 with the exception that a solution containing 0.1% by weight of sulphonated oil additive was used.

10 After the grafting the bath of 43 g/l concentration was cooled to 20°C and the viscosity of the bath was measured by a Höppler-type Rheo-Viskometer. The following results
15 were obtained.

Load	Viscosity
200 g	28.5 cP
150 g	37.5 cP
100 g	54.4 cP
20 50 g	102.2 cP

The viscosity of the starting solution of 50 g/l. concentration, in which gelling could not yet be observed, could be measured only at a load of 10 g. and under the above circumstances a value of 1.3 cP was obtained.

25 The above data unequivocally prove that the viscosity of the solution is of structural character.

30 The weight increase and other properties of the product corresponded to those obtained in Example 1.

Example 4

Grilon (Registered Trade Mark) monofilament was activated with a 3.5 Mrad dosage 35 of γ -radiation from a Co⁶⁰ source and was thereafter placed into a 10% aqueous acrylic acid solution having a viscosity of 86 cP at 20°C and under a shear stress of 50 g/cm² and was moved in circles in said solution at 40 60°C for 4 hours to effect grafting, the speed of movement being 6 metres per minute. Throughout this period, the reaction mixture was exposed to ultraviolet radiation.

45 The weight of the product obtained had increased by 65%. Its equilibrium humidity content was 9.5%, in contrast with the value of 4% observed with the untreated material.

50 When this process was repeated with the exception that the reaction mixture was not exposed to ultraviolet radiation during grafting, the weight of the product increased by only 30% and its equilibrium humidity content was only 6%.

Example 5

1 g of viscose fabric was activated with a 0.5 Mrad dosage of γ -radiation from a Co⁶⁰ source, and thereafter the activated fabric was placed into 18 ml of a 5% aqueous N-methylolacrylamide solution having a viscosity of 113 cP at a temperature of 20°C and under a shear stress of 50 g/cm², where it was moved in circles at 70°C to effect grafting, the speed of movement being 6 metres per minute. After 1.5 hours, 0.05 ml of 30% hydrogen peroxide were added to the solution and, after an additional 1.5 hours, the grafting was terminated. The samples were washed and thereafter cross-linked in the presence of an acid catalyst (MgCl₂) for 6 minutes at 160°C.

60 The weight of the product had increased by 20%. Although the tensile strength of the product had decreased by about 17%, the dimensional stability and the crease-recovery properties of the product had considerably improved.

WHAT WE CLAIM IS:—

1. A process for treating a fibrous material by forming active centres on said material and grafting onto said material a monomer containing an acryl group by moving said monomer through an aqueous solution of said monomer at a temperature below 100°C without damaging the gel structure formed in the solution and while applying a shear stress not greater than 300 g/cm², the solution having a viscosity of at least 1.2 cP at 20°C and at a shear stress of 10 g/cm² and not more than 300 cP at 20°C and at a shear stress of 50 g/cm².

2. A process according to claim 1, in which, following said process, said solution is replenished with water and with monomer and said process is repeated.

3. A process according to claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.

4. A fibrous material when treated by a process according to any one of the preceding claims.

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